

Confined and delocalized polarons in π -conjugated oligomers and polymers: A study of the effective conjugation length

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(Received 25 January 2004; revised manuscript received 15 March 2004; published 30 June 2004)

We studied optical absorption of polarons in π -conjugated oligomers and polymers using the photoinduced absorption technique as well as chemical doping spectra from the literature. We find that the photon energy of the polaron low-energy transition obeys a relationship that depends only on the oligomer-length in a wide class of unsubstituted and substituted oligomer solutions and films. Based on this observation, we show that polarons in polymer films can be either confined as in oligomers or quite delocalized, depending on the individual π -conjugated semiconductor. In high mobility polymer films polarons may be delocalized over several chains.

DOI: 10.1103/PhysRevB.69.241204

PACS number(s): 71.38.-k, 78.20.-e, 71.23.-k

Π -conjugated semiconductors have been used to manufacture promising thin film devices such as organic light-emitting diodes and field-effect transistors. It is well-known that chemical doping or electrical charge injection results in the formation of polarons in these systems.¹ Figure 1 shows a comparison between different models that have been used for describing polarons in π -conjugated semiconductors. Panel (a) depicts the electron-phonon (e-p) or Su-Schrieffer-Heeger (SSH) model.¹⁻³ It predicts that the e-p coupling causes a gap between valence and conduction band. In the singly charged system two localized polaron levels appear inside the gap. Experimentally one finds two optical transitions⁴ that are interpreted as the P_1 and P_2 transitions. Panel (b) depicts the molecular orbital picture where HOMO and LUMO are the highest occupied and lowest unoccupied molecular orbitals, respectively. These models are usually applied to a single, isolated chain; the effects of interchain interaction on polarons⁵⁻⁸ in real sample films are however not yet sufficiently understood.

Π -conjugated oligomers are often used as model compounds instead of π -conjugated polymers because they can be obtained with a well-defined chemical structure. Although the molecular weight of polymers is typically much larger than that of oligomers, nevertheless it is established that the polymer should be viewed as a string of effectively independent segments, separated by chemical or physical defects. The length of these segments is called the conjugation-length (CL).

We have used the continuous wave photoinduced absorption (PA) and the Fourier-transform infrared photoinduced absorption (FTIR-PA) spectroscopies to study the polaron optical transitions in films of π -conjugated polymers and oligomers. The PA spectroscopy has been widely used in π -conjugated materials, and experimental details were described previously.⁴ The PA spectrum, $\Delta\alpha(\omega)$ is obtained by dividing $-\Delta T/T$, where ΔT is the pump laser induced change in transmission. We extended the probe photon energy down to 0.05 eV using a FTIR spectrometer in combination with a deuterated triglycine sulfide (DTGS) detector. The FTIR-PA setup is described in more detail in Ref. 6.

Figure 2 shows the PA spectra of two π -conjugated polymer films, namely methylated ladder-type poly-para-phenylene [mLPPP, panel (a)] and poly-phenylene-vinylene [PPV, panel (b)] and that of an alkyl-substituted oligothiophene film [12T, panel (c)]. All these spectra show three optical transitions (it is known that the high energy transition in PPV is actually composed of two bands⁹). It is well-established⁴ that these transitions are due to triplet exciton absorption (T_1) and polaron absorption (P_1 and P_2).

Figure 3 shows the peak photon energies of the P_1 transition in a large variety of oligomers versus the oligomer-length, L .¹⁰ We note that the Δ , \circ , \oplus , \square , and ∇ data were taken from the literature.¹¹⁻¹⁵ It is seen that the P_1 transition in each of the oligomer classes redshifts as L increases; specifically $P_1 = P_{1,\infty} + \text{const}/L$. This observation in itself is not novel. In fact this scaling relation is ubiquitous in oligomers: the optical gap (i.e., the singlet exciton energy),¹⁶ triplet exciton energy,¹⁷ and also the P_2 transition each obey such a scaling relationship. *The striking observation is that if the P_1 data for the various oligomers are plotted versus L rather than the number of repeat-units (as it is usually done) and combined into a single graph, we find that the Δ , \circ , \square , \boxtimes , and ∇ data points all fall on a "universal" line.* This observation is fully appreciated when compared to similar plots

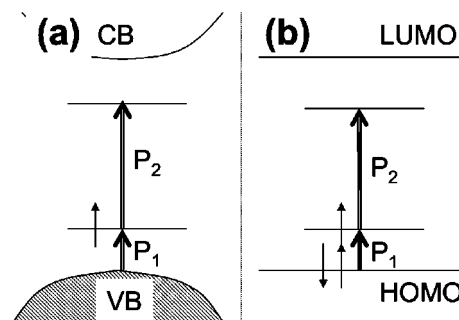


FIG. 1. Models used to describe polaron levels and optical transitions depicted here for the positive polaron. (a) Electron-phonon (SSH) model. (b) Molecular orbital picture.

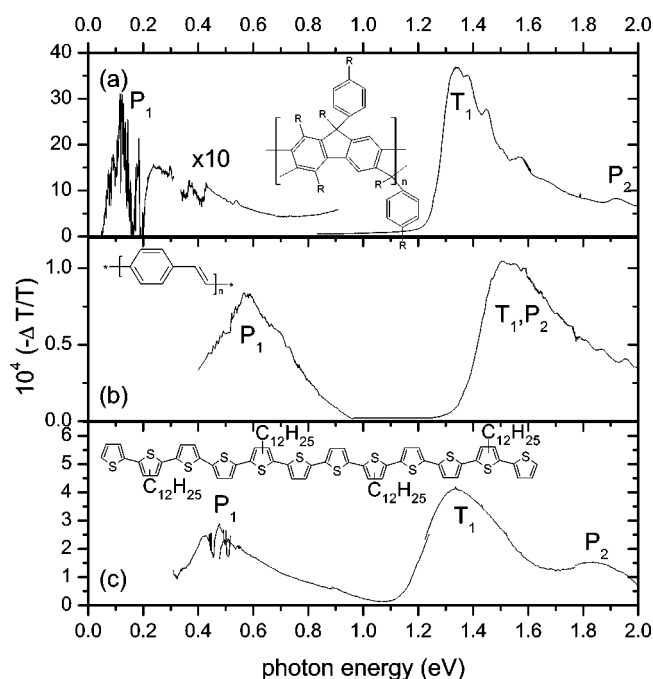


FIG. 2. PA spectra of π -conjugated polymer and oligomer films. (a) mLPPP (the chemical structure is given in the inset), (b) PPV (see inset), and (c) 12T (see inset). The spectra were measured at 80 K under excitation by an argon-ion laser (typically 100 mW) and modulated by an optical chopper (typically at 1 kHz). The T_1 transition is due to triplet-triplet absorption, whereas P_1 and P_2 are due to polaron absorption bands.

for the optical gap, where large differences between the various oligomer classes exist (e.g., 4 eV for 5P, but 3 eV for 5T). However, the data for the alkoxy-substituted OPV apparently do not follow the “universal” scaling law.

Figure 3 encompasses both anion and cation data. This suggests that anion and cation absorption are very similar. Indeed, in 3PV it was found that the difference between anion (reduced using potassium in THF solution), and cation (oxidized using SbCl_5 in CH_2Cl_2) absorption bands is less than 10 meV.¹⁸ Since both unsubstituted and alkyl-substituted oligomers display the same trend in Fig. 3, this indicates that alkyl-substitution has only minor effects on P_1 . Alkoxy-substitution on the other hand results in a major change of the cation absorption in OPV.¹³ This observation can be explained by the localization of the positive charge caused by alkoxy substitution.¹³ We may therefore conclude that the P_1 band scaling is universal for both anions and cations in a wide class of unsubstituted and alkyl-substituted oligomers.¹⁹ By extrapolation we find that $P_{1,\infty} = 0.25$ eV for the infinite oligomer.

In order to further expand the domain of validity of the “universal” scaling law for P_1 , PA measurements of P_1 in films of alkyl-substituted OT were performed and added to Fig. 3. It is seen that (a) the linear relationship for P_1 continues at least to OT with 17 repeat units, (b) interchain effects apparently do not play a significant role in OT, and (c) the fact that both positive and negative polarons are present in PA studies does not lead to a significant change of P_1 . These observations, together with the identification that

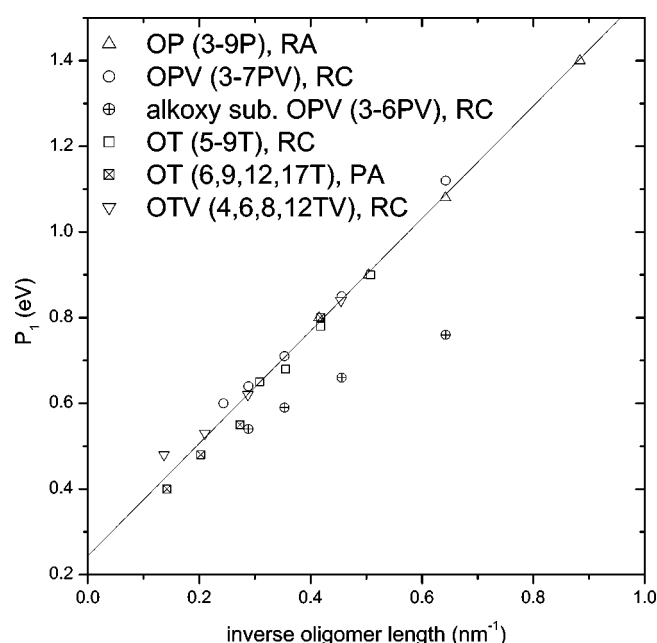


FIG. 3. The peak photon energies of the P_1 polaron transition in a variety of oligomers, namely solutions of (unsubstituted) oligophenyls [OP, Δ , radical anion (RA)], alkyl-substituted (AS) oligophenylene-vinyls [OPV, \circ , radical cation (RC)], alkoxy-substituted OPV (\oplus , RC), end-capped oligothiophenes (OT, \square , RC), films of AS OT (\boxtimes , PA), AS oligothiophene-vinyls (OTV, ∇ , RC). The solid line is a fit to the data excluding \oplus .

the CL of a polymer is the length of the “equivalent” oligomer, clearly suggest that P_1 can be used as a *universal and sensitive* measure of the CL of polymer films (caution is necessary when dealing with alkoxy-substituted polymers). Specifically, we may use the following method for obtaining the effective CL of polymer films: we measure P_1 , say by using the PA technique, then invert the universal relation $P_1(\text{CL})$.

This procedure is the basis for the presentation of the polymer P_1 data in Fig. 4, where crosses mark the data for a certain polymer (name is assigned). The y-coordinate of the crosses is equal to the measured P_1 using the PA technique, whereas the x-coordinate then yields the CL obtained by inversion of $P_1(\text{CL})$. We find that some polymer films [polyphenylene-ethynylene (PPE), PPV and regio-random poly-3-hexyl-thiophene (RRa-P3HT)] have a short CL and behave rather like oligomers, whereas in poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylene-vinylene] (MEH-PPV) we find that the polarons are considerably more delocalized than in oligomers. In addition, it is seen that this procedure does not yield a meaningful result for the CL for some polymer films for which $P_1 < P_{1,\infty}$. These polymers are regio-regular poly-3-hexyl-thiophene (RR-P3HT), mLPPP and poly(9,9-dioctyl)fluorene (PFO).²⁰ We note that the spectrum of PFO is for the so-called β -phase.^{21,22} It is clear that something interesting occurs in these samples. Before continuing this discussion, however, a closer look at the FTIR-PA spectra (Fig. 5) for these three polymers is in order.

It is seen that the P_1 transition is superimposed by narrow bands with some resemblance to the infrared active vibra-

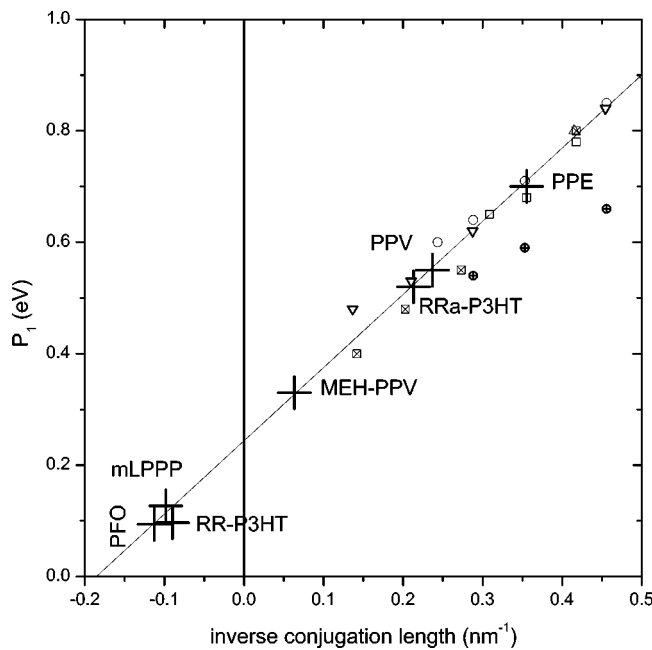


FIG. 4. The peak photon energies of the P_1 transition in a variety of π -conjugated polymer films, the names of which are assigned. The crosses mark the intersect with the linear fit to the oligomer data in Fig. 3; the y-coordinate therefore gives the measured P_1 peak photon energy, whereas the x-coordinate gives the effective conjugation length.

tions (IRAV) bands, that are well-known from the study of other polymers.¹ However, a more detailed examination of Fig. 5 indicates that the narrow superimposed features appear to have negative absorption contributions (antiresonances, ARs) rather than peaks as for regular IRAVs. Indeed, it has been shown that the sharp ARs are due to Fano-type interferences that occur when the P_1 transition overlaps with the vibrational spectrum.^{6,23} The P_1 transition is therefore given as the envelope of the measured spectrum, indicated by the dotted lines in Fig. 5.

We start our discussion with the SSH or e-p model that yields^{2,3}

$$P_1 = \frac{1 - \frac{1}{\sqrt{2}}}{2} E_g \times f(\gamma). \quad (1)$$

$f(\gamma)$ is a monotonously decreasing function such that $f(0) = 1$ and $f(\infty) = 0$, γ is the so-called confinement parameter and measures the degree of nondegeneracy of the ground state in π -conjugated systems. This model therefore predicts a strong correlation between the gap energy, E_g and P_1 . Our experimental findings are in stark contrast to this prediction; we find that P_1 is apparently completely independent of E_g .

The most generic model for polarons is the molecular crystal or Holstein model;² it is however not expected to be applicable in a quantitative way to π -conjugated polymers. This model yields for the " P_1 " transition²

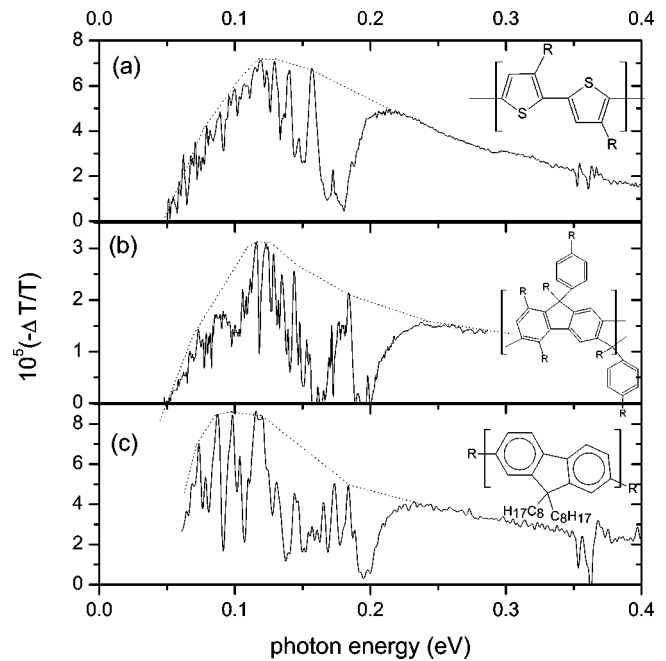


FIG. 5. The FTIR-PA spectra of the DP_1 transition for (a) RR-P3HT, (b) mLPPP, and (c) PFO. The spectra were measured at 10 K under excitation by an argon-ion laser (typically 100 mW), by subtracting 5000 scans of illuminated and unilluminated FTIR transmission spectra.

$$P_1 = \left(\frac{A^2}{2M\omega_E^2} \right)^2 \frac{1}{W}. \quad (2)$$

Here A quantifies the e-p coupling strength (e.g., in $\text{eV}/\text{\AA}$), M is the ionic mass, ω_E is the Einstein phonon frequency, and W is the band width before inclusion of e-p coupling. The term in the bracket is the energy, V associated with the e-p coupling.²⁴ The observation of the universal scaling law, $P_1 = P_{1,\infty} + \text{const}/L$ translates into the following statements. W is similar for a wide class of π -conjugated polymers and oligomers. Since W increases only weakly with L , then V is considerable larger in short oligomers but does not vanish even in the infinitely long oligomer. We note that a recent theoretical paper concluded that $V = \text{const}/N$ in a more or less universal manner in acenes and fullerenes with various numbers, N of π -bonds.²⁴

The inclusion of interchain interaction in theoretical calculations is generally found to destabilize the polaron^{5,7,25} since the amplitude of the e-p interaction decreases with increasing number of atoms involved.²⁴ However, even in the presence of interchain interaction it is also expected that polarons are restabilized by defects or finite CL.^{25,26} One therefore expects that this destabilization is only effective in high purity, ordered and rigid systems. We recall that mLPPP and β -phase PFO (Refs. 21 and 22) are particularly rigid polymers and that RR-P3HT forms nanocrystal lamellae because of its high regioregularity.^{6,27} It has been predicted that, for t_\perp on the order of 0.15 eV, the polaron excitation substantially delocalizes over adjacent chains.⁵ This leads to the expectation that the P_1 transition of a delocalized polaron (hereafter referred to as DP_1) is redshifted compared to the (hypothetical) value without interchain interaction. Therefore

delocalization as a result of interchain interaction can naturally explain the observation that $P_1 < P_{1,\infty}$. However, interchain interaction in the form of (transition) dipole-dipole interaction leads to a level-splitting and may result in a blueshift compared to the transition without level splitting.^{7,8} Nevertheless, an overall red-shift is consistently found in calculations.^{5,8} We may therefore conclude that $P_1 < P_{1,\infty}$ is the signature of delocalized polarons in RR-P3HT, mLPPP, and PFO. Since charge carrier mobilities in RR-P3HT,²⁷ mLPPP²⁸ and PFO (Ref. 29) are orders of magnitude larger than in PPV and RRA-P3HT films, it appears that delocalized polarons may be a necessary prerequisite for high mobility in polymers. We note that whereas evidence for delocalized polarons in RR-P3HT was found earlier,^{6,27,30} the present work succeeds to embed these results into a more general framework.

It has been predicted²⁵ that the polaronic effect may entirely disappear because of interchain interaction unless stabilized by defects or small CL. In this case the absorption of charge carriers would have to be described in a picture similar to that used for amorphous semiconductors.³¹ In this picture “ DP_1 ” is a transition between localized states below and

extended states above the mobility edge, respectively, and therefore a measure of the energy difference between quasi-Fermi level and mobility edge, respectively.

In summary, we found that the polaron P_1 transition obeys a universal relationship that depends only on the oligomer-length in a wide class of oligomer solutions. Employing the PA technique, we generalized this result to films of oligomers and polymers. We have therefore discovered a simple and sensitive method for measuring the effective CL in polymer films. Applying our methods to polymers, we find that polarons may be as confined as in oligomers in some systems, but may even be delocalized over several chains in high mobility polymer films.

We thank R. A. J. Janssen, R. D. McCullough, U. Scherf, and M. DeLong for supplying materials. We thank E. Ehrenfreund and R. Österbacka for fruitful discussions. The work at the University of Utah was supported in part by the NSF DMR 02-02790 and DOE DE-FG02-04ER46109 grants. M.W. acknowledges funding by Carver 8 50152 00 and University of Iowa, MPSFP 8 50029 55 grants.

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¹⁰OP-lengths are based on quaterphenyl (Ref. 32): intra-ring bond = 1.4 Å; inter-ring bond = 1.45 Å. OPV-lengths are based on trans-stilbene (Ref. 33): intra-ring bond = 1.39 Å; inter-ring single (double) bond is 1.45 Å (1.33 Å). OT-lengths are based on quaterthiophene (Ref. 34): intra-ring C-C bond = 1.411 Å; inter-ring bond = 1.45 Å. OTV length is based on thiophene ring and the vinyl bond length.

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¹⁹We limit our discussion to oligomers of nondegenerate ground-state polymers. In polyenes (oligomers of the degenerate ground

state polymer polyacetylene), the $P_1(L)$ scaling is a little steeper than that of the oligomers reported here, and $P_{1,\infty} = 0.1$ eV (Ref. 35). This may be interpreted as evidence that the polarons are somewhat more extended in polyenes.

²⁰RR-P3HT is closely related to the alkyl-substituted OT, whereas mLPPP and PFO are related to the OP; their P_1 should therefore follow from extrapolation of the OT and OP data, respectively.

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